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MOLECULAR PROCESSES IN COMETS

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Final Report

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Principal Investigator

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Report

1. Photodissociation of cometary molecules.

A major effort was expended in developing procedures for calculating by quantum-mechanical methods the cross sections for the photodissociation of the hydroxyl radical OH. The molecule OH is the primary dissociation product of water and observations of OH when combined with a determination of the lifetime of OH in the solar radiation field can be used to calculate the rate of release of water from comets.

There are many possible photodissociation channels whose efficiency depends upon the details of the spectrum of the radiation. We have calculated the potential energy curves of all the states of OH that can be reached by electric dipole absorption from the ground $X^2\Pi$ state by photons with energies up to about 12eV. Figure 1 is an illustration of them. The $X^2\Pi$ and $A^2\Sigma^+$ curves were obtained by Langhoff, van Dishoeck, Wetmore and Dalgarno (1982), the $^2\Sigma^-$ curves by van Dishoeck, Langhoff and Dalgarno (1983) and the $1^2\Delta$, $2^2\Pi$ and $3^2\Pi$ curves by van Dishoeck and Dalgarno (1983).

The Figure suggests that direct absorption into the repulsive $1^2\Sigma^-$ state will be an important participant in the photodissociation of OH. We have calculated the transition dipole moment and the resulting absorption cross sections (van Dishoeck, Langhoff and Dalgarno 1983). The corresponding cometary photodissociation rate at 1 AU from the Sun in conditions of average solar intensities is 2.2×10^{-6} s^{-1}. It is insensitive to the heliocentric velocity.

Absorption into the discrete vibrational levels of the $A^2\Sigma^+$ state followed by predissociation is still more efficient and in contrast to the $^2\Sigma^-$ absorption it does depend on the heliocentric velocity (Jackson 1980). We have worked out in detail the cometary destruction rates and find rates between 3.5 and 6.7×10^{-6} s^{-1} for heliocentric velocities between -60 and +60 km s^{-1} at a distance of 1 AU from the Sun (van Dishoeck and Dalgarno 1984).

We calculated the rates also for the deuterated molecule OD and obtain values of about 4.7×10^{-7} s^{-1} (Singh, van Dishoeck and Dalgarno 1983).

Absorption into the $2^2\Pi$ and $3^2\Pi$ states is a potentially important photodissociation pathway. The $2^2\Pi$ and $3^2\Pi$ states are strongly coupled by the interaction of the nuclear and electronic motions and the conventional single channel description adopted in studies of photodissociation is inadequate. We generalized the standard theory into a multichannel formulation and introduced a method in which the ab initio adiabatic states are transformed into diabatic states. In applying the theory we found many interesting resonance energy level structures (van Dishoeck, van Hemert, Allison and Dalgarno 1984).

We incorporated all these theoretical data in a comprehensive study of the radiative lifetimes of OH and OD in comets (van Dishoeck and Dalgarno 1984). The resulting OH lifetimes are shown in Fig. 2. The study pointed out that $O(^1D)$ was an important product of the photodissociation of OH by solar radiation and that photodissociation produced energetic hydrogen atoms.

We carried out a similar analysis of the photodissociation of CH and CD. These turn out to be much simpler. The lifetime does depend on the heliocentric velocity. The calculated values (Singh and Dalgarno 1987) are shown in Fig. 3.

The various methods and procedures we have developed were then applied to the photodissociation of NH, the values in the literature being evidently incorrect.

2. The second negative system of O_2^+

The possibility was raised that O_2^+ ions might be present in cometary tails and detectable through fluorescent scattering of sunlight. Transition probabilities of the various bands were needed. We used quantum chemistry methods to calculate the potential energy curves of the $X^2\Pi_g$ and $A^2\Pi_u$ states that are involved. From the eigenfunctions we obtained the transition dipole moment and transition probabilities. There are interesting changes in the lifetimes of vibrational levels because high lying vibrational levels of the ground electronic state lie energetically above low lying vibrational levels of the excited electronic state (Wetmore, Fox and Dalgarno 1984).

3. Radiative properties of molecular hydrogen

In response to requests from Drs. Yuk Yung, J. M Ajello and D. Shemansky in connection with the interpretation of Voyager ultraviolet spectrometer data, we embarked on a series of calculations of radiative transition probabilities of molecular hydrogen, a program that is continuing.

We calculated first the transition probabilities and spectral distribution of the $X^1\Sigma^+{}_g$-$B'^1\Sigma^+{}_u$ transition

(Kwok, Dalgarno and Posen 1985) and proceeded to study transitions between triplet states. We looked in particular at the $a^3\Sigma_g^+$ - $b^3\Sigma_u^+$ transition which gives rise to a continuous emission. We encountered difficulties in the correct determination of the transition moment at large internuclear distances which were finally overcome. Fig. 4 compares our theoretical predictions with experiments of Lishawa, Feldstein, Stewart and Muschlitz (1985). Our detailed prediction for individual vibrational levels have been published (Kwok, Guberman, Dalgarno and Posen 1986).

We have incorporated these data into detailed predictions of the emission spectrum produced by impact of electrons of various energies. Some of these spectra are illustrated in Fig. 5.

We also investigated the $c^3\Pi_u$ - $a^3\Sigma^+{}_g$, $i^3\Pi_g$ - $c^3\Pi_u$ and $i^3\Pi_g$ - $b^3\Sigma^+{}_u$ transitions and have constructed tables of the radiative transition probabilities for all vibrational levels of interest. The extensive results will appear in a paper by S.L. Guberman and A. Dalgarno in Physical Review A.

During the period of this grant A. Dalgarno wrote an invited review on the Photochemistry of Planetary Atmospheres (Dalgarno 1988) and was the principal organizer of the IAU symposia on Astrochemistry (Dalgarno, 1987, 1992) in which the connection between comets and the interstellar medium play a major role.

Figure Captions

Fig. 1: Calculated potential energy curves of the doublet states of OH.

Fig. 2: The lifetime τ against photodissociation of OH as a function of the heliocentric radial velocity v of the comet. The dotted curve refers to absorptions into the $A^2\Sigma^+$ state only. The short-dashed curve refers to absorptions into the $A^2\Sigma^+$ and the $1^2\Sigma^+$ states at solar maximum. The long-dashed curve refers to absorptions into all states at solar minimum and the full curve to absorptions in all states at solar maximum. The open circles show the lifetimes inferred from UV observations with their uncertainties indicated. KBM: Comet Kobayashi-Berger-Milon (1975IX) (Festou 1981b); Br: Comet Bradfield (1979X) (Weaver et al. 1981a); Be: Comet Bennett 1970II) (Keller and Lillie 1974); K: Comet Kohoutek (1973XII) (Festou 1981b).

Fig. 3: The lifetime τ in seconds of CH as a function of the heliocentric velocity in km s^{-1}.

Fig. 4: The spectral irradiance $\lambda^{-1}\omega_\lambda$ of H_2 in arbitrary units measured by Lishawa et al. (1985) and predicted for emission from the $v'' = 0$ level of the $a^3\Sigma_g^+$ state. The points • and o are the measured values for electron impact energies of 11.60 eV (•) and 11.75 eV (o) respectively.

Fig. 5a-5f: The continuum emission arising from the excitation of the $a^3\Sigma_g^+$ state by the impact of electrons for various energies. Each curve is labelled by the electron energy in eV.

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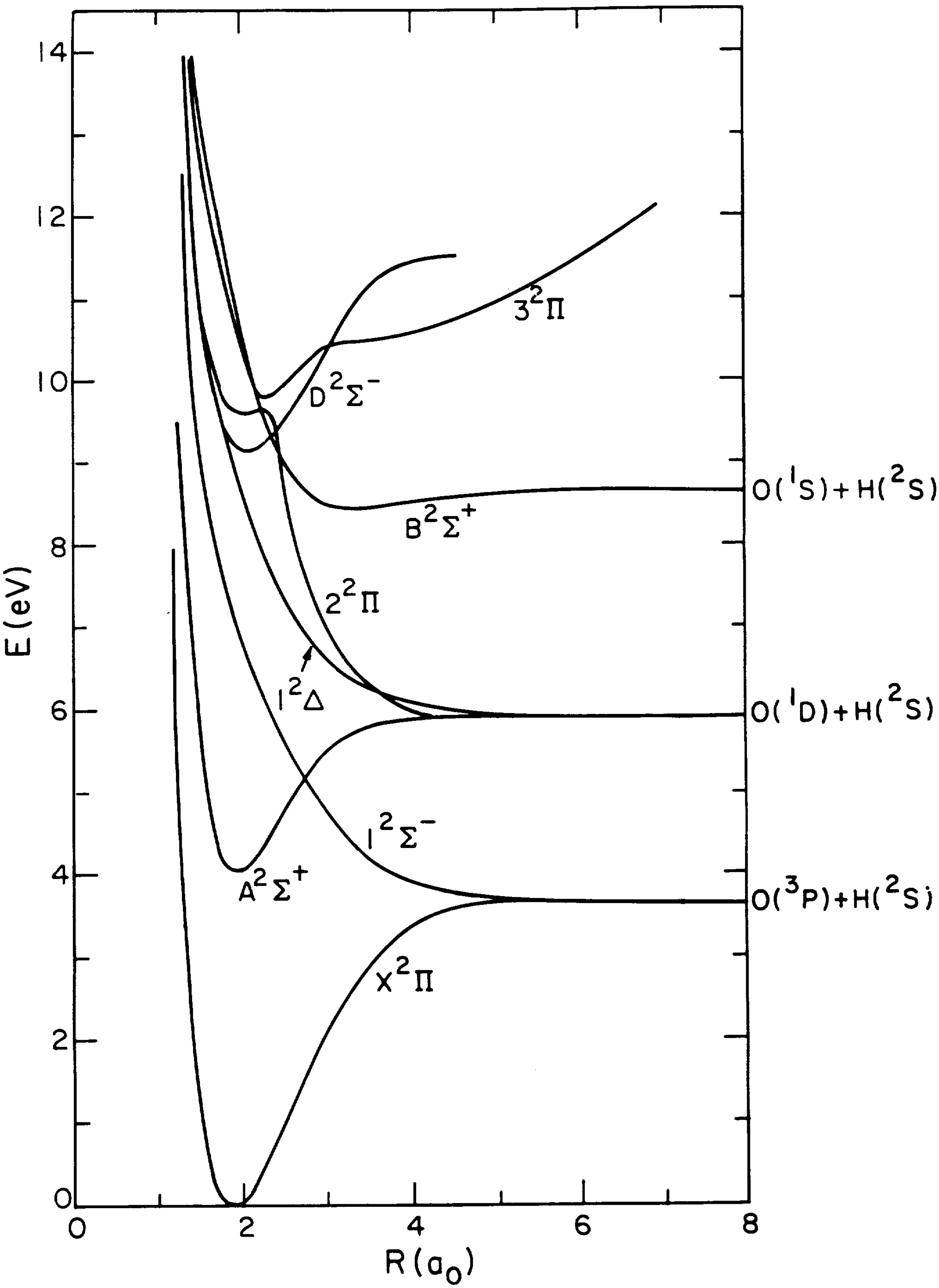
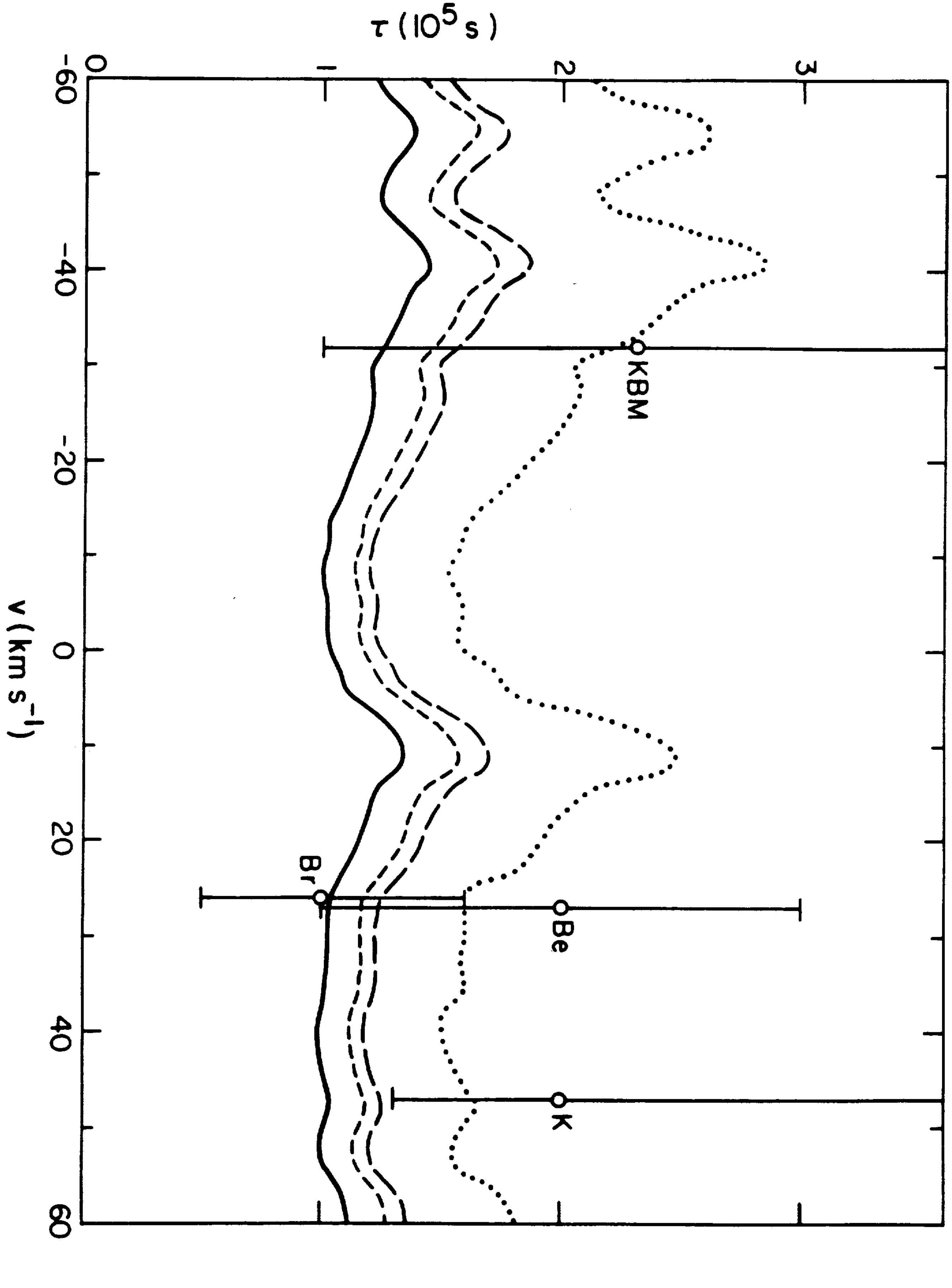
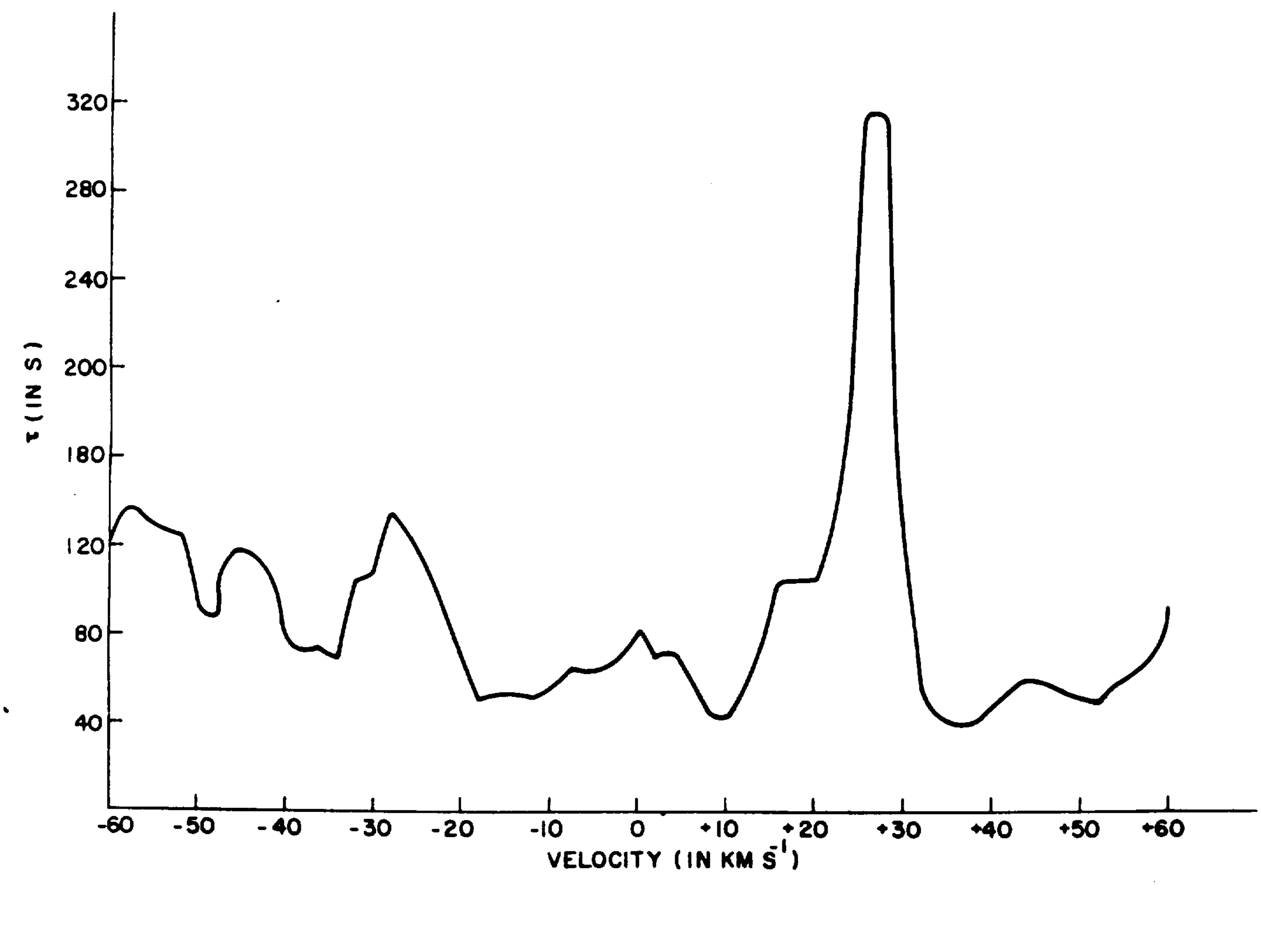
Fig. 1



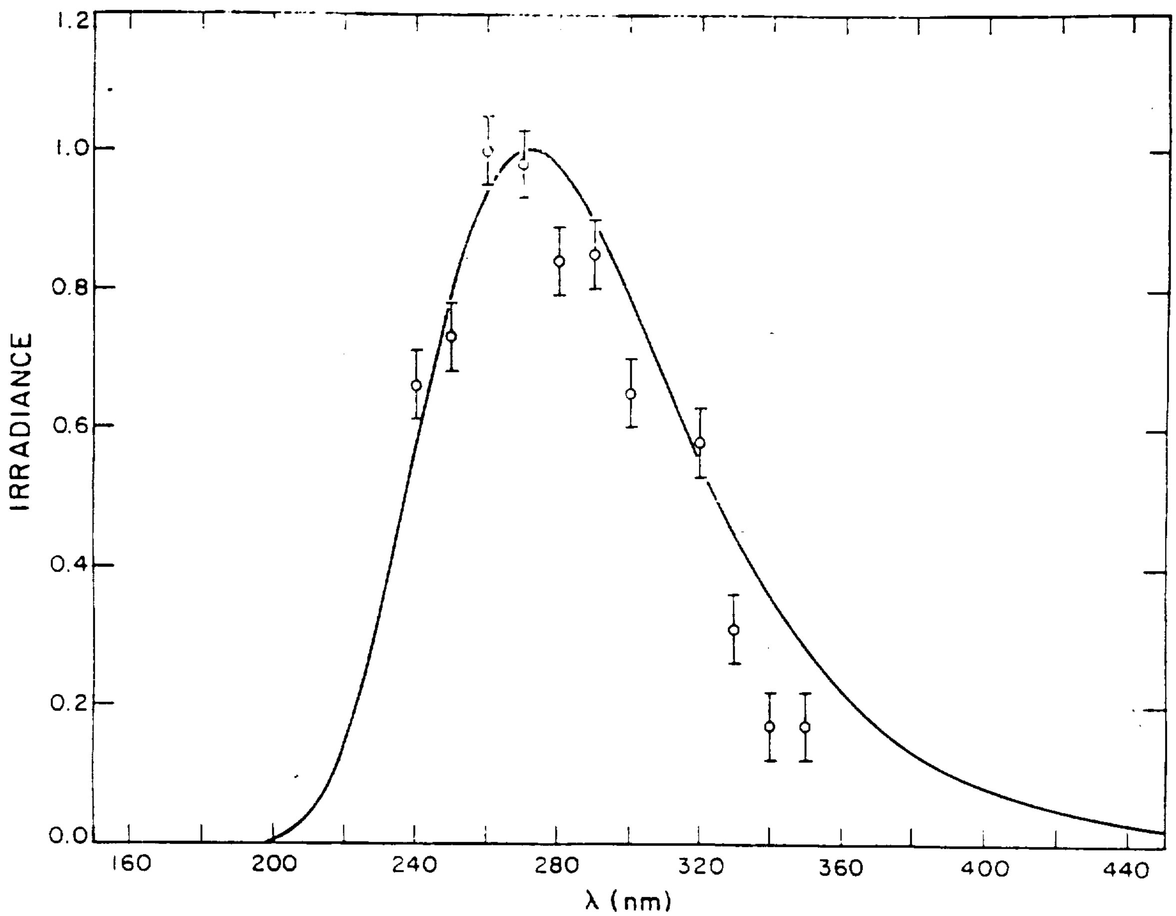
E (eV)
R (a$_0$)
0
2
4
6
8
10
12
14
$3^2\Pi$
$D^2\Sigma^-$
$B^2\Sigma^+$
$2^2\Pi$
$1^2\Delta$
$1^2\Sigma^-$
$A^2\Sigma^+$
$X^2\Pi$
O(^{1}S) + H(^{2}S)
O(^{1}D) + H(^{2}S)
O(^{3}P) + H(^{2}S)

Fig. 2





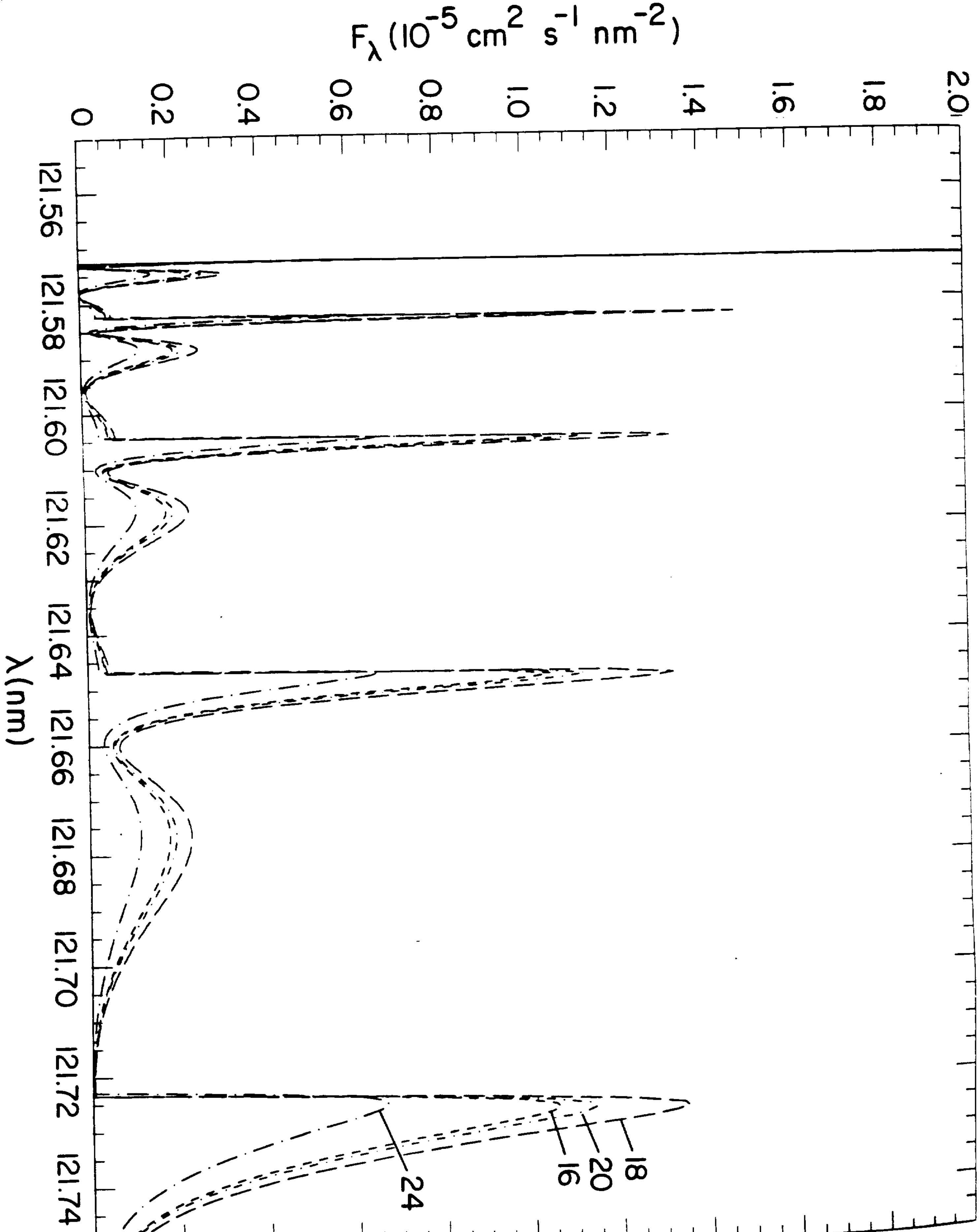
The lifetime τ in seconds of CH as a function of the heliocentric velocity in km s^{-1}



1.2
1.0
0.8
0.6
0.4
0.2
0.0
IRRADIANCE
160
200
240
280
320
360
400
440
λ (nm)

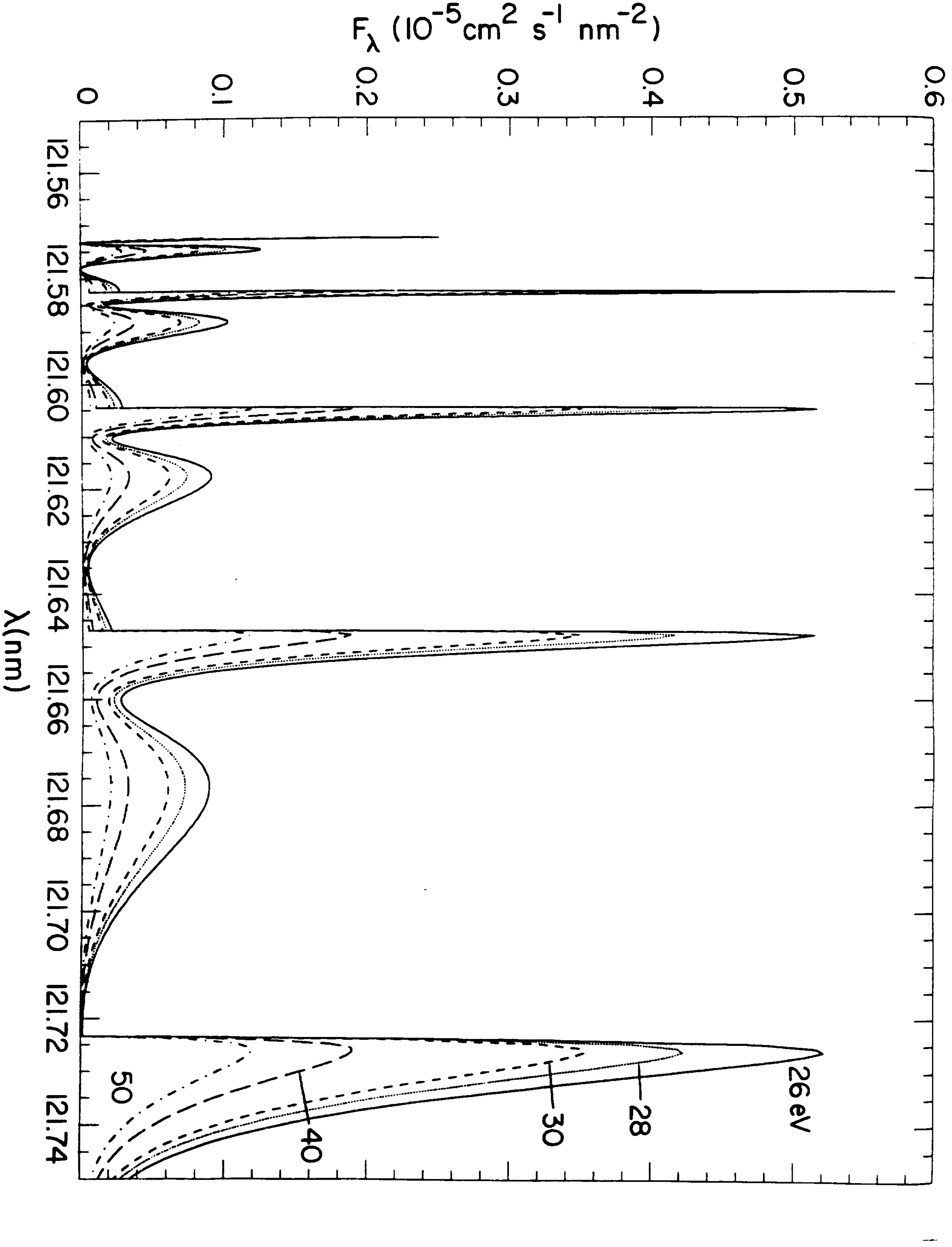
Fig. 4

Fig. 5a



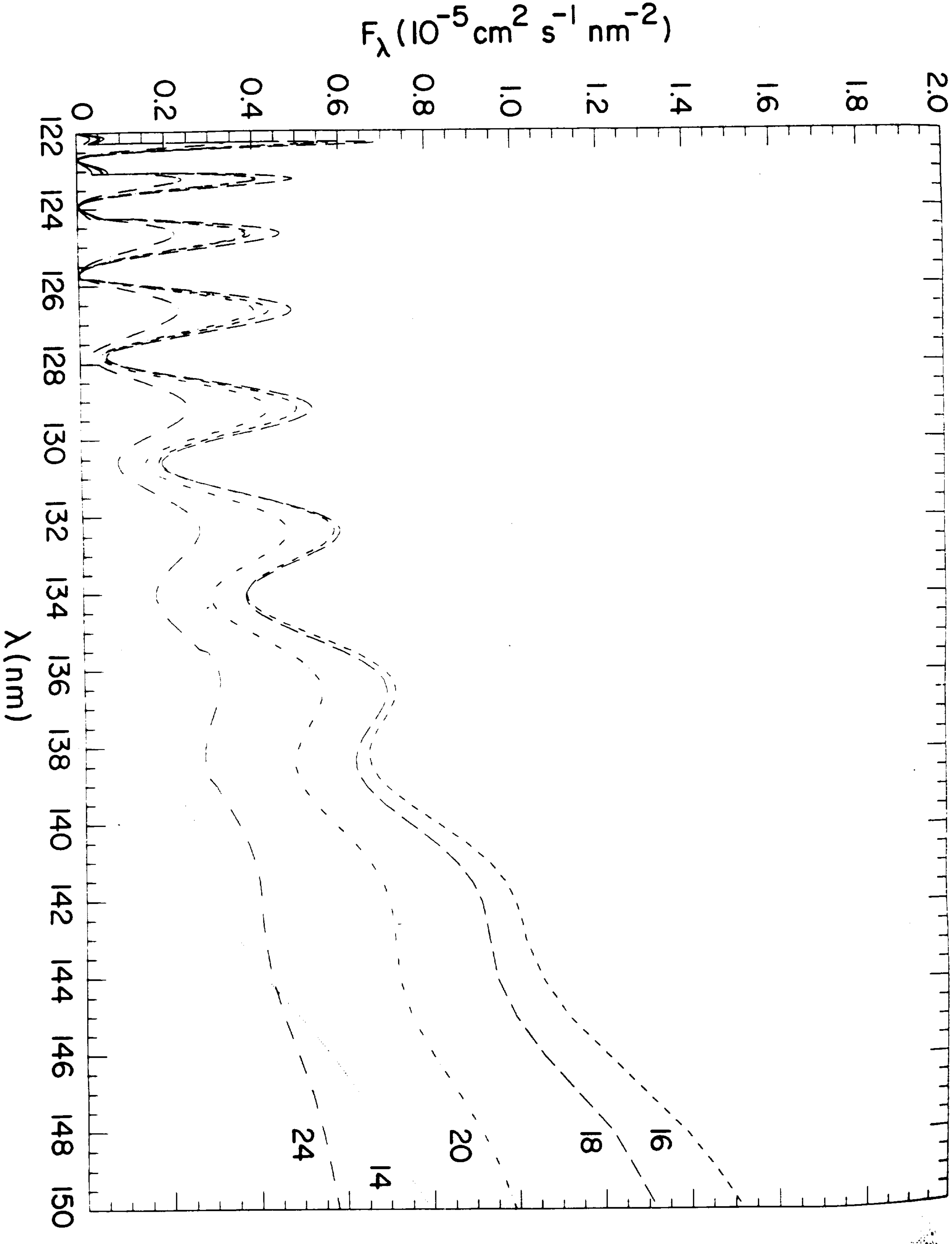
$F_\lambda\,(10^{-5}\,cm^2\,s^{-1}\,nm^{-2})$
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
121.56
121.58
121.60
121.62
121.64
121.66
121.68
121.70
121.72
121.74
λ(nm)
24
16
20
18

Fig. 5b



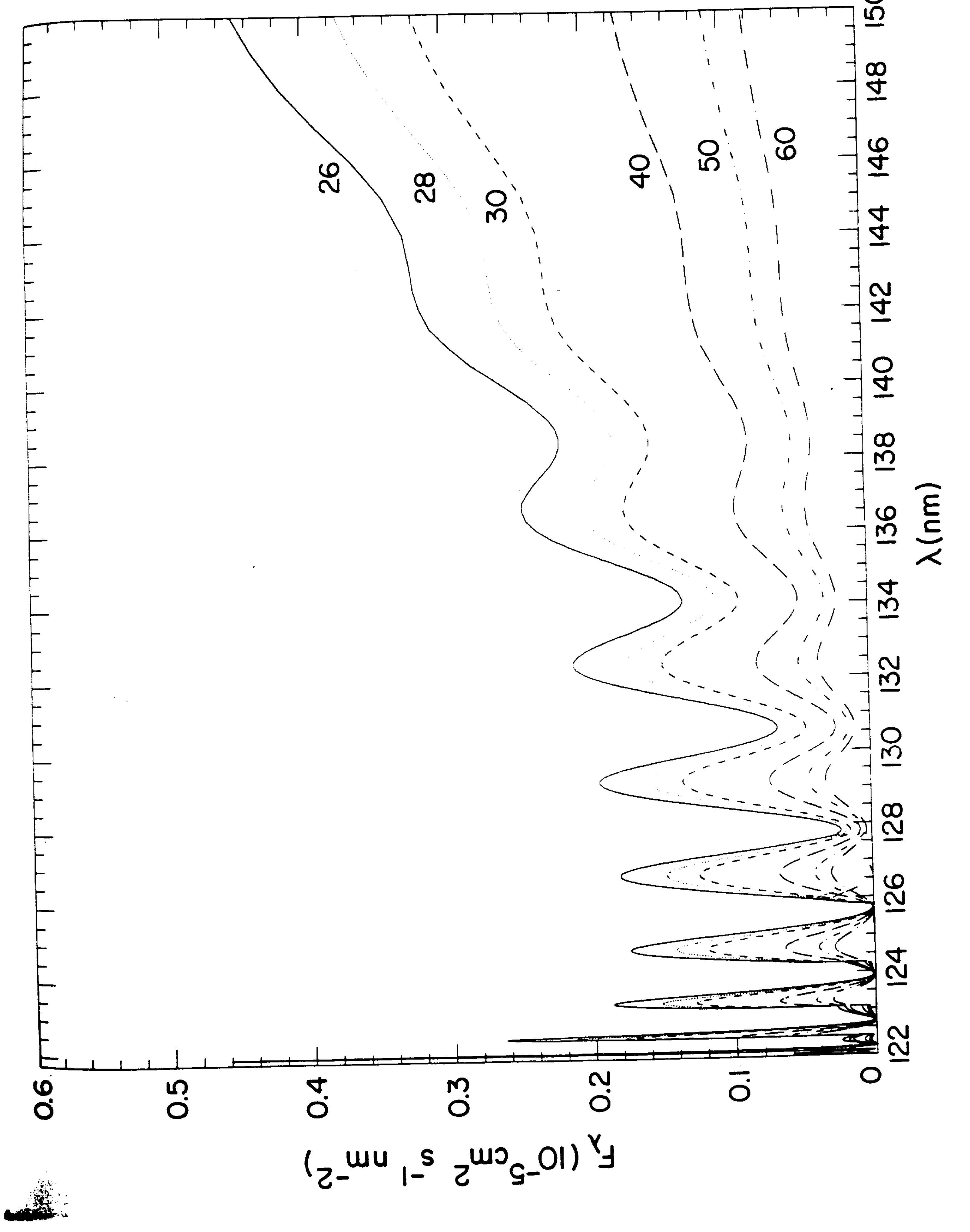
F_λ (10^-5 cm^2 s^-1 nm^-2)
0
0.1
0.2
0.3
0.4
0.5
0.6
121.56
121.58
121.60
121.62
121.64
121.66
121.68
121.70
121.72
121.74
λ(nm)
26eV
28
30
40
50

Fig. 5c



Fλ(10-5 cm2 s-1 nm-2)
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
122
124
126
128
130
132
134
136
138
140
142
144
146
148
150
λ(nm)
16
18
20
24
14

Fig. 5d



0.6
0.5
0.4
0.3
0.2
0.1
0
122
124
126
128
130
132
134
136
138
140
142
144
146
148
150
λ(nm)
F_λ (10^{-5} cm^2 s^{-1} nm^{-2})
26
28
30
40
50
60

Fig. 5e

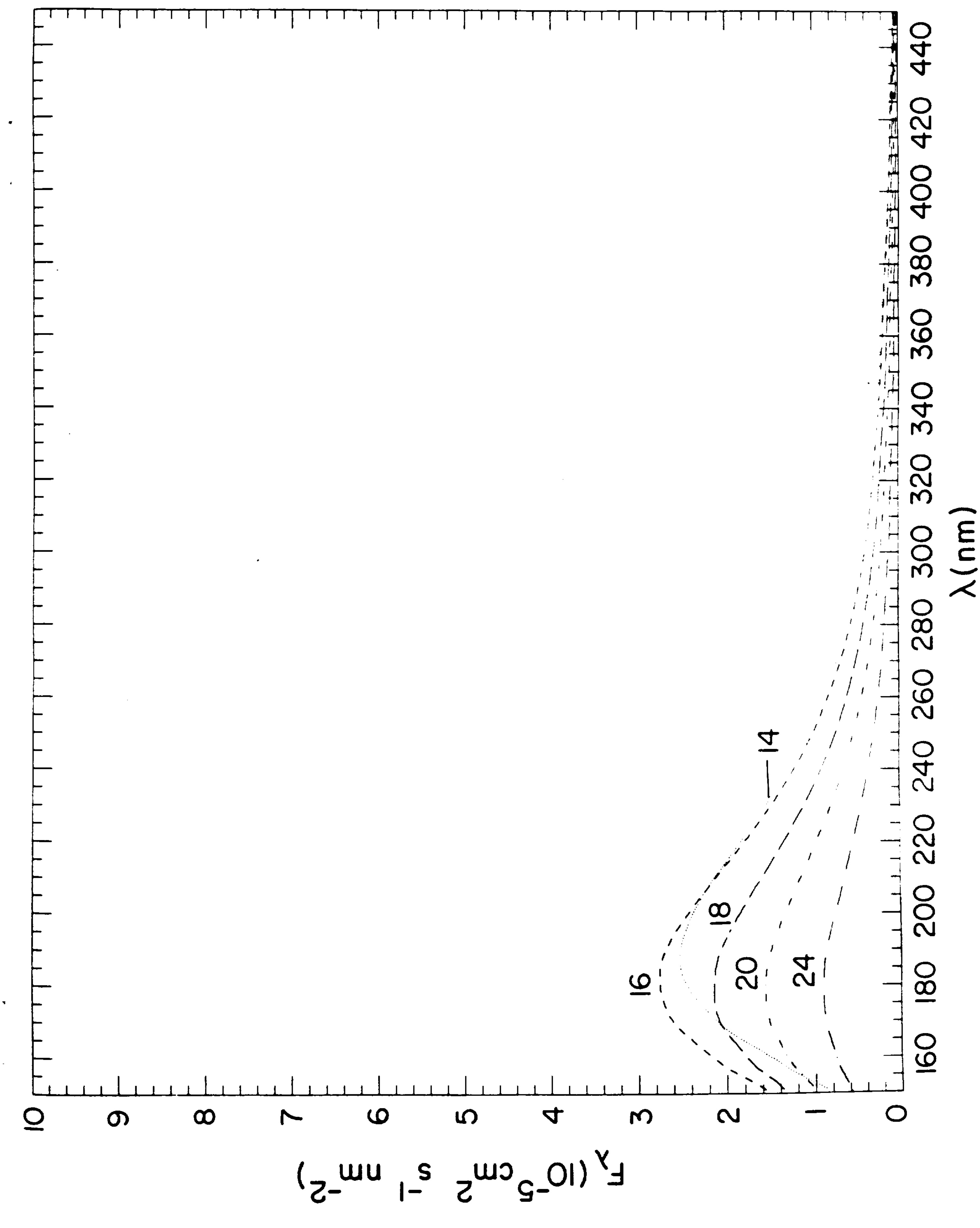


Fig. 5f